Journal of Sciences, Islamic Republic of Iran 15(3): 277-282 (2004)
University of Tehran, ISSN 1016-1104

Residual Stress in Cu Sputtered Films on Glass Substrates at Different Substrate Temperatures

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Abstract

Copper films of 300 nm thickness deposited by planar magnetron sputtering on glass substrates, for substrate temperatures between 300 and 500 K, and deposition rate of 10 $Ås^{-1}$. Microstructure of these films was obtained by X-ray diffraction, while the texture mode of diffractometer was used for stress measurement by the $\sin^2\psi$ technique. The components of the stress tensor are obtained using measurements at three different ϕ angles of 0, 45 and 90 degrees by proposed technique in this work. The relation between stress in these films and the processes in film growth through structure zone model (SZM) is explained.

Keywords: Residual stress; Stress tensor; X-ray diffraction; Thin Cu films

1. Introduction

Thin films are ubiquitous of modern technology, with uses spanning the range from the decorative gold plating on jewelry to the various metallization levels on ULSI chips. The physical properties of the thin film layers depend strongly on their microstructure parameters such as the degree of crystallinity, crystallographic orientation, crystallite size, elastic and plastic strain fields, etc. figure prominently in the design, development, and failure analysis of devices containing thin films.

One important feature which arises in the physical vapor deposition (PVD) is the porosity of thin films. Electron microscope studies of surfaces and cross sections of thin films have revealed that many metals and most dielectrics form thin films with columnar microstructure. The Structure Zone Model (SZM) consisting of three zones, separated by two boundary temperatures, proposed by Movchan and Demchishin [1] for the broad description of polycrystalline film structure, and refined by Thronton [2] for coatings of metals produced by sputtering, in which an additional zone (transition zone T) appears between zone I and zone II, has been under further refinements by many investigators [3-6]. Messier [7] proposed a model of the internal void networks as an attempt for quantification of thin film morphology for films deposited under low mobility conditions, as a fractal construction based upon the random competition for cone growth. Kaiser [8] reviewed the fundamentals of thin film growth, considering nucleation, coalescence and thickness growth processes, while Burne [9] has given a comprehensive review on microscopic view of epitaxial metal growth considering nucleation and aggregation processes. In our earlier works, the influence of different deposition parameters on the structure of UHV deposited erbium, copper and zinc films were reported and agreements with SZM were obtained [10-12].

In this work, the influence of substrate temperature and film thickness on the mechanical properties

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(strain/stress) of copper (fcc) films sputter deposited onto glass substrates is reported, and the relation between stress in these films and the microstructure of the films proposed by SZM is explained. Cu is usually used as decorative coatings and thin film circuits as well as being a good candidate for studying surface diffusion of adatoms on metal surfaces.

Among the various methods used for strain/stress determination, X-ray diffraction (XRD)-based techniques play an important role because they are phase specific, non-contact, and nondestructive. Furthermore, these techniques simultaneously yield other relevant information such as crystallographic orientation, presence of other phases, composition, etc. that are essential in the interpretation of stress/strain data [13]. Noyan *et al*. [14] have given a very comprehensive review on the measurement of the residual stress in thin film structures with X-ray techniques and have discussed the interpretation of the data obtained and their relationship to mechanical reliability.

2. Experimental Details

Copper (an fcc metal) films of different thickness were produced by planar magnetron sputtering from copper targets on glass substrates at different temperatures. The purity of copper sputtering targets was 99.9%. A HINDIVAC coating plant with a base pressure of 10^{-6} Torr was used. The argon gas (99.995%) pressure for the plasma formation was 3×10^{-2} Torr for sputtering Cu. Discharge voltage was 450 V with a 0.4 A current for the sputtering of Cu. For the sputtering of Cu films the optimum distance between the cathode and the substrates was found to be 9.0 cm. Cover-glass wafers (approximately 25 mm × 25 mm × 0.15 mm) were used as substrates. The substrates were fixed by stainless steel masks on the substrate holder, which was heated to a set temperature as required in each run. The substrate temperature was controlled by programmed thermostats and thermocouples fixed inside holes on the surface of substrate holder near to the substrates.

Just before use all glass substrates were ultrasonically cleaned in heated acetone then ethanol. The surface texture of the substrates was measured by a Talystep or a Talysurf profilometer. The rms substrate roughness R_q for glass substrates was 0.3 nm. Film thickness was monitored by a quartz crystal unit and measured by a Talystep profilometer. The deposition rate was 10 $Ås^{-1}$ for deposition of Cu.

Details of the samples presented are given in Table 1 as well as the predicted Structure Zone Model (SZM) zone to which the films belong [1,2].

Table 1. Details of Cu/glass samples examined

Sample No.	Substrate temperature T_s	T_s/T_m	Thickness	SZM zone
Cu4	320 K	0.24	300 nm	I
Cu5	381 K	0.28	300 nm	I
Cu6	411 K	0.30	300 nm	I
Cu7	445 K	0.33	300 nm	II

The analysis of the above samples provides the opportunity to investigate the influence of substrate temperature on the residual stresses developed in thin Cu films. The $\sin^2\psi$ method was implemented, using a Philips XRD X'pert MPD Diffractometer with Eulerian ATC cradle to obtain both phase scan and the data at three ϕ angles of 0°, 45° and 90° and six ψ angles up to $\sin^2\psi = 0.75$. The (111) and (200) lines for Cu samples were analyzed. The components of the stress tensor are obtained using a new method proposed in this work, in which only ψ^+ measurements are required.

3. Results

The X-ray method for determination of residual stress in crystalline materials is based on the measurement of inter-planar spacing *d* at various tilts, ϕ and ψ, to the X-ray beam, Figure 1. In a polycrystalline specimen, only those grains properly oriented to diffract at each tilt contribute to the diffraction profile. This selectively implies that the elastic constants connecting the measured strain (or change in inter-planar spacing) to the stresses will vary with the particular set of planes (*hkl*) chosen for measurement [13,14].

Typical sets of the X-ray diffraction lines' profiles obtained for Cu4 (111 line) sample for different angles are given in Figure 2. The fits shown in Figure 2, use a Gaussian plus a level background. By obtaining the lattice spacing, $d_{\phi\psi}$ from the proper diffracted peak position for a given reflection *hkl*, (for different ψ 's, and at three fixed ϕ (0°, 45° and 90°), the strain along $L_{\phi\psi}$ may be obtained from [14],

$$\begin{aligned}\left(\varepsilon_{33}^{L}\right)_{\phi\psi} &= \frac{d_{\phi\psi}-d_0}{d_0} = \mathbf{M}_{3i}^{SL}\mathbf{M}_{3j}^{SL}\varepsilon_{ij}^{S} \\ &= \varepsilon_{11}^{S}\cos^2\phi\sin^2\psi + \varepsilon_{12}^{S}\sin 2\phi\sin^2\psi \\ &\quad +\varepsilon_{22}^{S}\sin^2\phi\sin^2\psi + \varepsilon_{33}^{S}\cos^2\psi \\ &\quad +\varepsilon_{13}^{S}\cos\phi\sin 2\psi + \varepsilon_{23}^{S}\sin\phi\sin 2\psi\end{aligned} \tag{1}$$

where d_0 is the (hkl) lattice spacing of the strain-free (*e.g.*, Cu) powder sample and **M**s are transfer tensors from $\mathbf{S_i}$ (sample) system to $\mathbf{L_i}$ (laboratory) system (Figure 1). The incident beam, the diffracted beam, and the normal to the diffracting planes $\mathbf{L_3}$ are in the same plane. $\mathbf{S_3}$ is normal to the sample surface and $\mathbf{S_1}$ and $\mathbf{S_2}$ are in the sample surface. The sample can be rotated on the diffractometer in ϕ and in ψ . In other word, in practice one may equally define ψ as a "roll" about an axis lying along the intersection of the plane of the substrate with the X-ray incidence plane. Equation (1) is the fundamental formula of X-ray strain determination [13-14]. In polycrystalline materials, it is expected to obtain three possible basic types of $d_{\phi\psi}$ *vs.* $\sin^2\psi$ curves (*i.e.*, linear "regular" which can be explained directly by Equation (1); ψ splitting "split" that can arise as a result of triaxial stress, in which both ψ^+ and ψ^- should be measured and analysis to be carried out [13-15]; and "oscillatory" behavior, which is associated with strong texture [14,15]. The "split" behaviour can be modeled by the final two terms in equation (1), while "oscillatory" behaviour requires a substantially different analysis.

Our strain data obtained for Cu films for only ψ^+, show splitting behavior for some films and nearly linear for other Cu samples (three typical examples for different ϕ angles are given in Figure 3 for (111) line), the (200) line of Cu samples showed similar patterns as (111) line.

We have applied a different analysis method, which is in a sense different from the normal procedure carried out for ψ splitting data analysis that involves averaging the strain over ψ^+ and ψ^- data. In the proposed method in this work, for obtaining the strain tensor components only one ψ direction (*i.e.*, ψ^+ or ψ^-) measurement is required.

We may re-write Equation (1) in the following form;

$$\left(\varepsilon_{33}^{L}\right)_{\phi\psi} = \frac{d_{\phi\psi} - d_0}{d_0} = \mathbf{M}_{3i}^{SL}\mathbf{M}_{3j}^{SL}\varepsilon_{ij}^{S}$$

$$= \alpha x + 2\beta\sqrt{x\left(1-x\right)} + \gamma \qquad (2)$$

$$x = \sin^2\psi$$

$$\alpha = \varepsilon_{11}^{S}\cos^2\phi + \varepsilon_{12}^{S}\sin 2\phi + \varepsilon_{22}^{S}\sin^2\phi - \varepsilon_{33}^{S}$$

$$\beta = \varepsilon_{13}^{S}\cos\phi + \varepsilon_{23}^{S}\sin\phi$$

$$\gamma = \varepsilon_{33}^{S}$$

Now, by fitting this function to the experimental points, one can obtain α,β,γ coefficients. Then, having known α,β,γ at $\phi = 0$ we may obtain $\varepsilon_{11},\varepsilon_{13},\varepsilon_{33}$, and at $\phi = 90°$ and $\phi = 45°$ we may obtain $\varepsilon_{22},\varepsilon_{23}$ and ε_{12}, respectively. This procedure was carried out, and the curves (solid lines) in Figures 3 are the results of this analysis. We also found that despite the linear appearance of some experimental data for Cu films, this function (Equation 1) fits to the data better than the linear function (examined by least square fitting method). Hence, one may claim that all six components of the strain tensor are non zero, but ε_{13} and ε_{23} are relatively smaller than the other components. The components of the strain tensor obtained, using this method, for all Cu ((111) and (200) lines) films. Table 2 gives the components of the stress tensor obtained using this data in Equation 3,

$$\left(\varepsilon_{33}^{L}\right)_{\phi\psi} = \frac{d_{\phi\psi} - d_0}{d_0}$$

$$= \frac{1+\nu}{E}\left\{\sigma_{11}^{S}\cos^2\phi + \sigma_{12}^{S}\sin 2\phi + \sigma_{22}^{S}\sin^2\phi - \sigma_{33}^{S}\right\}\sin^2\psi + \frac{1+\nu}{E}\sigma_{33}^{S}$$

$$-\frac{\nu}{E}\left(\sigma_{11}^{S} + \sigma_{22}^{S} + \sigma_{33}^{S}\right)$$

$$+\frac{1+\nu}{E}\left\{\sigma_{13}^{S}\cos\phi + \sigma_{23}^{S}\sin\phi\right\}\sin 2\psi \qquad (3)$$

Using the value 129.8 GPa for the Young's modulus, E and 0.343 for Poisson ratio, ν for Cu [19].

3. Discussions

Figures 4 (a-b) show the variation of stress components *vs.* reduced temperature (T_s/T_m), for Cu(111) and Cu(200) lines, respectively. In Figures 4 (a and b), there exists a maximum value at $T_s/T_m = 0.3$ for tensile stress, while at lower temperature the tensile stress relaxes to an almost constant value, and at higher temperatures than ($T_s/T_m = 0.3$) the stress relaxes towards probably a zero value or compressive stress.

We may divide Figures 4 (a and b) into three regions ($T_s/T_m < 0.28$; $0.28 < T_s/T_m < 0.3$; $T_s/T_m > 0.3$) and find relation (s) with the structure zone model (SZM) according to what follows;

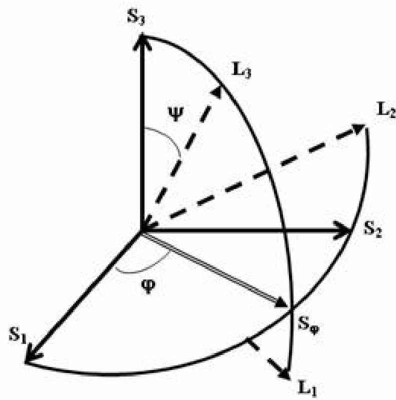


Figure 1. Definition of the coordinate system for the specimen $\overline{\mathbf{S}}_i$ and the laboratory system $\mathbf{L}_i$. The incident beam, the diffracted beam, and the normal to the diffracting planes $\overline{\mathbf{L}}_3$ are in the same plane. The sample can be rotated on the diffractometer in ϕ and in ψ. S_3 is normal to the sample surface, and S_1 and S_2 are in the sample surface.

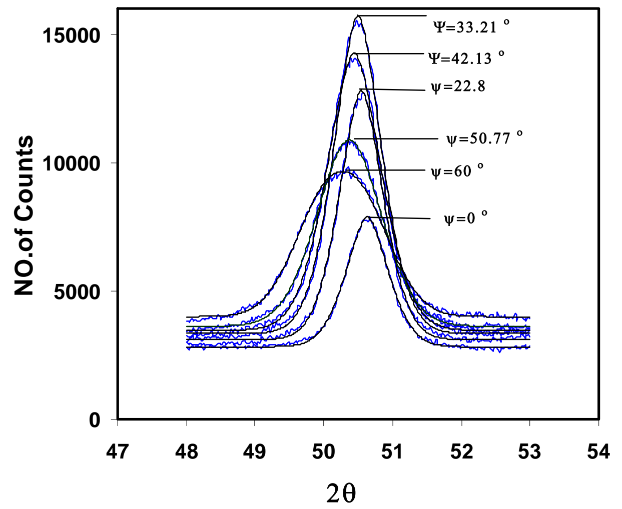


Figure 2. X-ray diffraction lines' profiles for Cu4 (111) sample for different ψ angles.

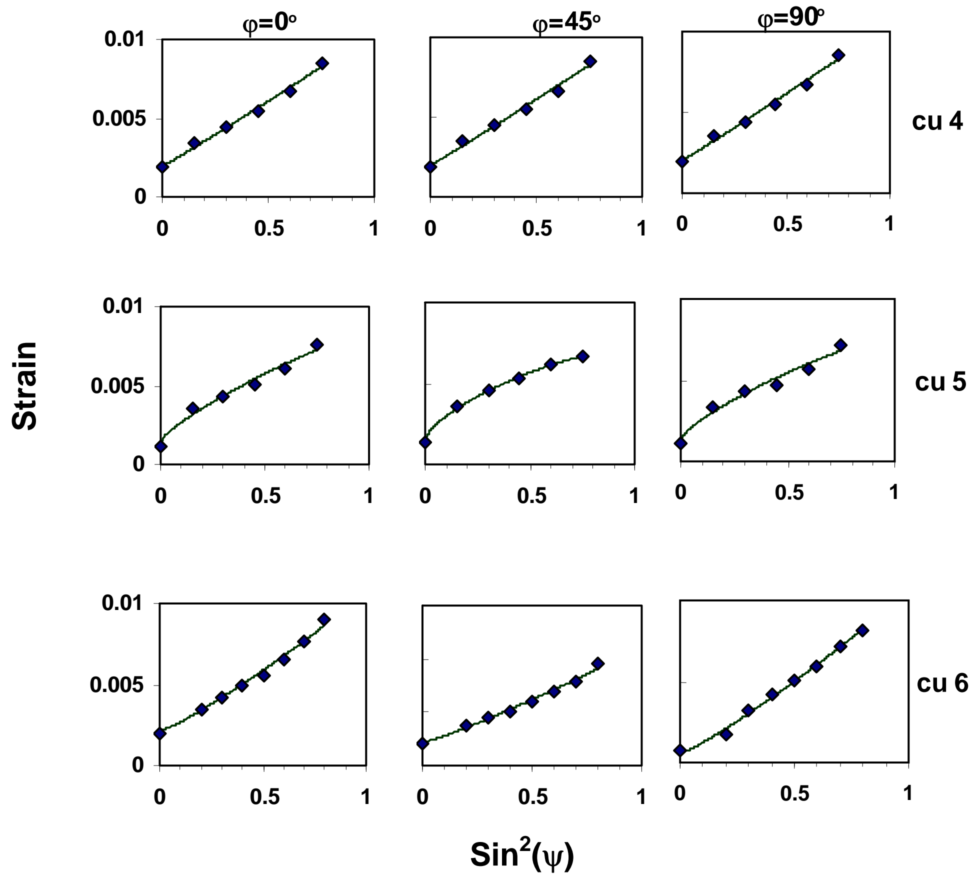


Figure 3. Strain in Cu films obtained from (111) line, as a function of $\sin^2\psi$ measured at three different ϕ angles of 0°, 45° and 90°.

Table 2. Components of the stress tensor (GPa) for Cu sputtered films on glass substrates at different substrate temperatures

Sample Name	(h k l)	Thickness (Å)	T_s/T_m	Components of stress tensor (GPa)					
				σ_{33}	σ_{11}	σ_{13}	σ_{22}	σ_{23}	σ_{12}
Cu4	(1 1 1)	3000	0.24	2.733±0.226	3.577±0.275	-0.076±0.048	3.724±0.284	-0.079±0.039	-0.027±0.005
Cu5	(1 1 1)	3000	0.28	2.225±0.317	3.060±0.395	0.057±0.058	3.02±0.404	0.059±0.058	0.008±-0.005
Cu6	(1 1 1)	3000	0.30	4.376±0.415	5.64±0.511	-0.095±0.087	5.638±0.521	-0.090±0.077	-0.009±0.005
Cu7	(1 1 1)	3000	0.33	1.543±0.209	2.283±0.267	0.025±0.039	2.284±0.267	0.038±0.039	0.005±0.001

i) In the first region (T_s/T_m < 0.28), we have observed a constant tensile stress. This may be related to Zone I structure of (SZM) of sputtered thin films, with a tapered structure with voids between grains, in which, considering the energy of adatoms and the Argon gas pressure [20], one expects to observe a competition between compressive and tensile stresses.

ii) In the second region (0.28 < T_s/T_m < 0.3), in which the tensile stress reaches its maximum value, can be regarded as Zone T, in which a closed packed fibrous structure is predicted.

iii) Region three (T_s/T_m > 0.3), at the boundary between Zone I/Zone T and Zone II, as it is discussed by many authors [*e.g.*, 4], the increase in the substrate temperature causes activation of other processes (*e.g.*, diffusion, causing reduction in the number of defects, which in turn reduces the void fraction in the film, and resulting in denser films) in thin film structure and yields columnar structure. Therefore, one expects the relaxation of tensile stress, and formation of compressive stress, as it may be concluded from Figures 4 (a and b).

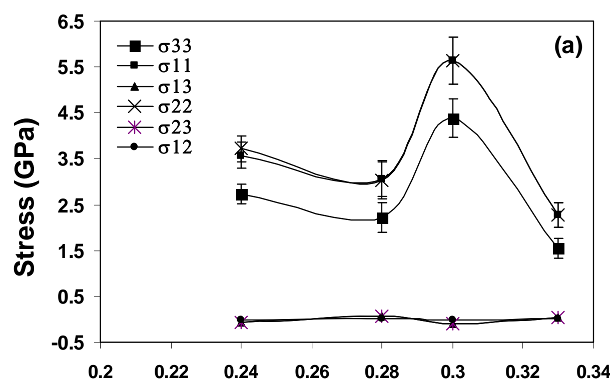
An interesting feature is the small value obtained for the normal component to the surface (σ_{33}) relative to the surface components (σ_{11}, σ_{22}), which can be related to the exposed side (surface) of the layer. It is also worthwhile to mention that value of the shear components of stress (*i.e.*, $\sigma_{12}, \sigma_{13}, \sigma_{23}$) are too small (~zero GPa) relative to the values of the main components (*i.e.*, $\sigma_{11}, \sigma_{22}, \sigma_{33}$) (~2-6 GPa) of stress (see Figures 4 (a and b) and Table 2).

4. Conclusions

Copper films produced by sputtering technique on glass substrates at different substrate temperature, were analyzed, using $\sin^2\psi$ method for obtaining components of stress tensor and micro-structural information. In this method, the diffraction peaks' patterns were only measured at ψ^+ angle and fitted to a mathematical function corresponding to Equation 2. When the measurements were carried out at three different ϕ angles, namely 0, 45 and 90 degrees for a scan over ψ angles, one can obtain all components for stress tensor.

Acknowledgements

This work was carried out with the support of the University of Tehran. The authors are grateful to Messers M.M. Saffari and M. Yousefi and Ms. Fardindost of the Faculty of Science, of Tarbiat Modares University for their help with the XRD measurements.



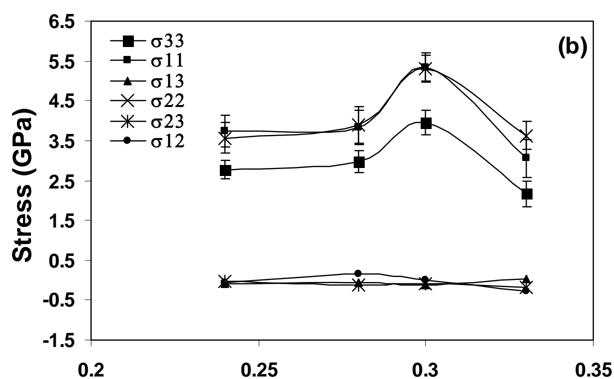


Figure 4. Stress components for Cu films as a function of reduced temperature. a) Cu(111); b) Cu(200).

References

1. Movchan B.A. and Demchishin A.V. *Phys. Met. Metall.*, **28**: 83 (1963).
2. Thornton J.A. *J. Vac. Sci. Technol.*, **12**: 830 (1975).
3. Messier R. and Yahoda J.E. *J. Appl. Phys.*, **58**: 3739 (1985).
4. Grovenor C.R.M., Hentzell H.T.G., and Smith D.A. *Acta Metall.*, **32**: 773 (1984).
5. Hentzell H.T.G. and Smith D.A. *J. Vac. Sci. Technol.*, **A2**: 218 (1984).
6. Messier R., Giri A.P., and Roy R.A. *Ibid.*, **A2**: 500 (1984).
7. Messier R. *Ibid.*, **A4**: 490 (1986).
8. Kaiser N. *Appl. Optics*, **41**: 3053 (2002).
9. Burne H. *Surface Science Report*, **31**: 121 (1998).
10. Savaloni H., Player M.A., Gu E., and Marr G.V. *Vacuum*, **43**: 965 (1992).
11. Savaloni H. and Player M.A. *Ibid.*, **46**: 167 (1995).
12. Savaloni H. and Bagheri Najmi S. *Ibid.*, **66**: 49 (2002).
13. Noyan I.C. and Cohen J.B., In: *Residual Stress Measurement by Diffraction and Interpretation*. Springer-Verlag, New York (1987).
14. Noyan I.C., Huang T.C., and York B.R. *Critical Reviews in Solid State and Material Sciences*, **20**: 125 (1995).
15. Dolle H. *J. Appl. Cryst.*,**12**: 489 (1979).
16. Savaloni H., Gu E., Player M.A., Marr G.V., and Munro I.H. *Rev. Sci. Instrum.*, **63**: 1494 (1992).
17. Savaloni H., Player M.A., Gu E., and Marr G.V. *Ibid.*, **63**: 1497 (1992).
18. Player M.A., Shi Z., Clark S.M., Miller M.C., and Tang C.C. *Physica B*, **248**: 405 (1998).
19. Kaye G.W.C. and Laby T.H. *Tables of Physical and Chemical Constants **and Some Mathematical Functions***. Longman Science & Technology, London and New York, 386 p. (1986).
20. Hoffman D.W. and Thornton J.A. *Thin Solid Films*, **45**: 387 (1977).